

# The "Living" Stable Free Radical Polymerization - The Acrylate Conundrum

Michael K. Georges, Nancy A. Listigovers, Peter G. Odell, Gordon K. Hamer, Marion H. Quinlan, and Richard P. N. Veregin *Xerox Research Centre of Canada, 2660 Speakman Drive., Mississauga, Ontario, Canada L5K 2L1*

In 1993, it was reported, for the first time, that narrow polydispersity polystyrene could be obtained by a free radical polymerization process. Since then, the nitroxide mediated "living" stable free radical polymerization (SFRP) process has received considerable attention from us and others to define the mechanism and kinetics of the process, as well as, the types of molecular architectures that can be made and the range of monomers that can be used.<sup>2,14</sup> Clearly, the usefulness of the process will be defined by the different classes of monomers that can be polymerized. While the synthesis of styrenics and dienes were straightforward, acrylates represented a greater challenge. Obtaining high molecular weight, narrow polydispersity homopolymers of acrylates in which the molecular weight increased in an incremental and linear fashion remained elusive. Initially reactions with n-butyl acrylate provided oligomers that appeared to increase in molecular weight at a rate of one monomer unit per hour for the first few hours and then stop. Chain extensions reactions with acrylate using TEMPO-terminated polystyrene macroinitiators, which had repeatedly been used for chain extensions with styrene, also proved unsuccessful. These results were perplexing since narrow polydispersity random copolymers of styrene and n-butyl acrylate in high yields with acrylate feed compositions as high as 50% had always been possible. However, polymerizations with feed compositions above 50% gave poorer yields and the yields decreased as the monomer feeds approached 100% acrylate (Table 1).

In an attempt to understand these seemingly contradictory results, different aspects of the polymerization were studied in depth. One of the first things that needed to be demonstrated was whether a nitroxide, once it was attached to an acrylate, would dissociate and allow more monomer to add to the chain end. To study this issue, the SFRP process was used to synthesize a homopolymer of styrene and a quasi-block copolymer of styrene and n-butyl acrylate in which the acrylate block contained one to two units of acrylate. These materials were then used to identify the <sup>13</sup>C NMR peaks of the nitroxide methyl groups that could be differentiated on the basis of whether the nitroxide was attached to a styrene or acrylate monomer. The <sup>13</sup>C NMR spectrum of a random copolymer of styrene and n-butyl acrylate, synthesized with a 50% feed composition of n-butyl acrylate, showed TEMPO attached to styrene and acrylate end units. Chain extension of the random copolymer with styrene proceeded to provide a block copolymer in which the second block was homopolystyrene. More important, the <sup>13</sup>C NMR of the product showed that TEMPO was exclusively attached to styrene end groups, demonstrating that TEMPO does react reversibly with n-butyl acrylate to allow further introduction of monomer.

The initiation reaction of acrylates with AIBN and 4-oxo-TEMPO was also investigated to see how it may have been contributing to the acrylate problem. Since the mechanism of the SFRP process suggests that the initiating species is the adduct between the cyano isopropyl radical from AIBN and 4-oxo-TEMPO (Figure 1), the adduct was synthesized and characterized. Interestingly, the adduct was found not to initiate the polymerization of n-butyl acrylate although it did initiate the polymerization of styrene. In the case of n-butyl acrylate, the adduct was shown to decompose to 4-oxo-TEMPO and structure 2. Thus, initiating acrylates with AIBN in the presence of 4-oxo-TEMPO appeared to be one of the problems.

The amount of free nitroxide in the acrylate polymerizations was also monitored since it was known from the styrene system that free nitroxide levels affect the rate of polymerization. Whereas, in the polymerization of styrene, the free nitroxide concentration levels off

after initiation, the free nitroxide level in the polymerizations of acrylates goes down during initiation to a given level, but then increases. These results suggested that some process, probably some type of termination, was generating free nitroxide, and the free nitroxide concentration was rising to a level that inhibited the acrylate polymerization. If this were true, then the excess nitroxide, present after initiation, could be a problem. To explore this further, polymerizations were carried out with nitroxide-terminated polystyrene (PS-T) macroinitiators to ensure that there is approximately a one-to-one ratio between the propagating chains and free nitroxide. As illustrated in Figure 1, this approach proved to be quite successful. Macroinitiators could be extended with n-butyl acrylate to higher molecular weights in an incremental fashion while maintaining narrow polydispersities. The lowest molecular weight peak is the polystyrene macroinitiator, and the two subsequent peaks correspond to the product after one and two hours, respectively. Polystyrene macroinitiators (Mw = 1.7K) have been chain extended with acrylate to molecular weights as high as 75K. If the polymerizations are performed in the presence of 3-indole butyric acid, an acid that promotes livingness in plants by stimulating root formation, resins of higher molecular weights and narrower polydispersities are obtained compared with a control without acid (Figure 2).

In summary, the problem of polymerizing acrylates by the SFRP process has been resolved. Studying different aspects of the polymerization provided insight that facilitated a better understanding of the mechanism of the acrylate polymerization, allowing reaction conditions to be chosen that enabled the reaction to proceed successfully.

Table 1. Random Copolymer of Styrene/n-Butyl Acrylate with Varying Amounts of n-Butyl Acrylate

Acrylate	Styrene	Mn (K)	PDI	Yield
24	24.6	32.5	1.32	89
43	24.8	38.2	1.54	81
64	24.4	36.4	1.49	65
81	6.1	10.6	1.73	33

Figure 1. Adduct from Heating AIBN in the Presence of TEMPO

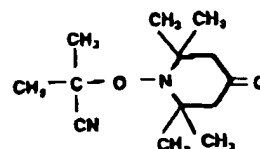
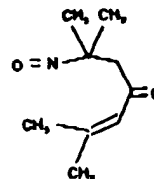
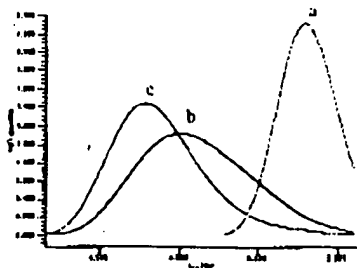
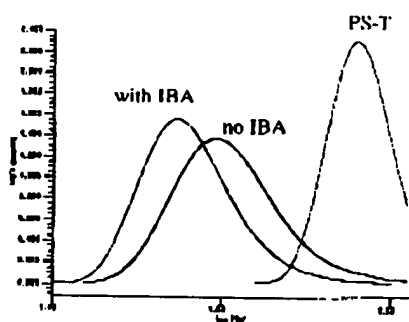


Figure 2. Decomposition Product of Cyanoisopropyl/4-oxo-TEMPO Adduct (Figure 1)





**Figure 1.** GPC for PS-T macroinitiation of n-butyl acrylate. Molecular weight increases from right to left. (a) polystyrene macroinitiator; (b) polymerization after one hour; (c) polymerization after two hours.



**Figure 2.** GPC for PS-T macroinitiation of n-butyl acrylate with and without 3-indolebutyric acid (IBA). Molecular weight increases from right to left.

#### References

1. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules*, **1993**, *26*, 2987-2988
2. Hawker, C. J.; Hedrick, J. L. *Macromolecules* **1995**, *28*, 2993-2995
3. Veregin, R. P. N.; Georges, M. K.; Hamer, G. K.; Kazmaier, P. M. *Macromolecules* **1995**, *28*, 4391-4398
4. Fukuda, T.; Terauchi, T. *Chemistry Let.* **1996**, 293-29

C